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Synthesis and characterisation of cobalt, nickel and copper complexes with tripodal 4N ligands as novel catalysts for the homogeneous partial oxidation of alkanes

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ABSTRACT

Four new compounds of the general formula $[M(L)(CH_3COO)][PF_6]$, where L is a tetradentate tripodal ligand such as tris[2-(dimethylamino)ethyl]amine (L1) or (2-aminoethyl)bis(2-pyridylmethyl)amine (L2) and M is Co(II), Ni(II) or Cu(II), have been prepared employing a simple two-step synthesis. The compounds have been characterised by elemental analysis, mass spectroscopy, IR spectroscopy and X-ray diffraction. The catalytic properties of the derivatives containing the aliphatic ligand L1 have been investigated in particular toward the oxidation of cyclohexane and adamantane in the presence of the sacrificial oxidant *m*-CPBA (*meta*-chloroperbenzoic acid). Good TONs and selectivity have been determined for the cobalt and nickel compounds.

1. Introduction

The development of efficient non-precious metal catalysts capable of oxidising saturated hydrocarbons under mild reaction conditions is a challenging goal in both synthetic and industrial organic chemistry. In nature, redox processes such as the selective hydroxylation of C–H bonds are catalysed at the active sites of iron or copper metal complexes are therefore promising candidates in the search for new homogeneous alkane oxidation catalysts. In this field, tripodal tetradentate ligands, such as tris(2-pyridylmethyl)amine (TPA) and its derivatives [2], containing both σ-donating tertiary amine and π-accepting pyridyl groups are versatile ligands and have been used for the preparation of various transition-metal complexes containing the group 5–11 elements, lanthanides, and an actinide.[1] These ligands have been employed for the design of structural and/or functional model complexes of mono- and dinuclear metalloenzymes [3] containing different metal sites as dioxygen activation centres. Even though iron complexes might be considered as the most promising candidates for biomimetic C–H bond hydroxylation, several other catalysts for alkane oxidation containing transition metals such as Mn, Co, Cu, Ru and Os instead of iron have also been successfully investigated [4–9]. Recently, a few publications showed that nickel chemistry could also be employed as a valid alternative to iron systems [10]. In particular, Itoh et al. have demonstrated that the Ni(II) complex $[Ni(TPA)(CH_3COO)(H_2O)](BPh_4)$ is a

cohol selectivity acid (*m*-CPBA) as an oxidant. These experiments also showed that the total TON (turnover number) of the Ni(II) complex was higher than that of Fe(II), Mn(II) and Co(II) complexes of the same ligand, and the alcohol-product selectivity of the Ni(II) complex was much better than that of the Fe(II) and Mn(II) complexes. Notably, orders of the catalytic activity (TON) (Ni > Fe > Co > Mn) and the alcohol-product selectivity (Co > Ni > Fe–Mn) of the complexes in the TPA-system were similar to the orders of the efficiency and alcohol-product selectivity in the gas phase reaction of methane with the first-row metal-oxo species $[MO]^+$ (M = Ni, Co, Fe, Mn) reported by Schwarz and co-workers [9]. The same group also pointed out recently that copper-based intermediates of the type $[CuO^{\cdot}]^+$ with a Cu(II) oxyl radical character show an excellent reactivity and selectivity toward hydrogen atom abstraction from inert hydrocarbons such as methane [11].

Later, Itoh and co-workers isolated a series of Ni(II) complexes of 3N, tripodal 4N and 3NO ligands and studied the effect of ligand and counter anion on the catalytic oxidation of cyclohexane with

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[1] The survey of the Cambridge Crystallographic Data Centre revealed that the crystal structures of the transition-metal complexes of TPA and erivatives of V, Cr, Mn, Re, Fe, Ru, Os, Co., Rh, Ir, Ni, Cu, Nd, Eu, Tb, Lu, and U have been reported.

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m-CPBA and suggested the involvement of the highly reactive nickel-oxo intermediate rather than an auto-oxidation type free radical species in the catalytic cycle. Also, the same group reported Ni(II) complexes of tripodal phenolate ligands, which are capable of catalysing the oxidation of cyclohexane to cyclohexanol using *m*-CPBA with up to 100% conversion based on the oxidant in solvent free conditions. Hikichi et al. crystallised the nickel(II) alkylperoxo complex [Ni(Tpipr)(OO*t*Bu)] and studied its oxidation activity towards substituted benzaldehydes [12]. However, the factors determining the selectivity as well as efficiency of the catalysts and the nature of intermediate species still remain unclear.

These promising results encouraged us to keep investigating this class of compounds. We focused our attention on the tripodal 4N ligands tris[2-(dimethylamino)ethyl]amine (Me_6TREN, L1) and (2-aminoethyl)bis(2-pyridylmethyl) amine (uns-penp, L2) (Fig. 1) and their Ni(II), Co(II) and Cu(II) derivatives. The catalytic activity of the aliphatic L1 ligand metal complexes toward the oxidation of different organic substrates, in the presence of *meta*-chloroperbenzoic acid (*m*-CPBA) as the oxidant, has been investigated in CH_3CN/CH_2Cl_2 mixed solvent systems. The Co(II) and Ni(II) systems show catalytic activity for the hydroxylation of alkanes such as cyclohexane or adamantane with good alcohol selectivity within one hour. Interestingly, unlike for the systems reported by Itoh [10a], the cobalt derivative reported here shows a higher TON than the nickel one, which, on the other hand, has a better selectivity.

2. Materials and methods/experimental

Commercially available materials were used without further purification. The ligands tris[2-(dimethylamino)ethyl]amine (Me_6TREN, L1) and (2-aminoethyl)bis(2-pyridylmethyl) amine (uns-penp, L2) have been prepared by slightly modification of the methodology reported in literature [13]. Elemental analyses were carried out at the Institut für Technologie Organischer Stoffe of the Johannes Kepler Universität, Linz. Mass spectra were recorded on a Finnigan LCQDecaXPplus Ion Trap Mass spectrometer with ESI ion source, and MALDI-TOF data were collected on a Bruker Autoflex III Smartbeam spectrometer, whereby a matrix:sample ratio of 10:1 was used. IR-measurements were carried out on a Shimadzu IRAffinity-1 device deploying the ATR technique (Specac Golden Gate). Single crystal structure analysis was carried out on a Bruker Smart X2S diffractometer with Mo Kα radiation (λ = 0.71073 Å). Further crystallographic and refinement data can be found in Table 1. The structures were solved by direct methods (SHELXS-97) [14] and refined by full-matrix least-squares on F^2 (SHELXL-97) [15]. The H atoms were calculated geometrically and a riding model was applied during the refinement process.

2.1. [Co (L1)(CH_3COO)][PF_6]·H_2O (**1**)

The first synthetic step was the preparation of [Co(Me_6TREN)(CH_3COO)](CH_3COO) by mixing $Co(CH_3COO)_2{\cdot}4H_2O$ (57 mg, 0,23 mmol) and Me_6TREN (in excess) followed by sonication until all the pink cobalt salt was transformed into a bright green oil. The excess of ligand was washed away with diethyl ether. The bis-acetate complex was then dissolved in the smallest possible amount of acetone containing KPF_6 in excess. When the two solutions were mixed the white by-product CH_3COOK started to precipitate. After filtration of the potassium acetate, the solvent was evaporated and the solid isolated was dissolved in dichloromethane in order to remove the excess of KPF_6. After filtration, the solution was dried under vacuum. The solid obtained was dissolved in methanol and the pure complex precipitated by addition of diethyl ether. Crystals suitable for XRD were grown at low temperature by slow diffusion of diethyl ether into a methanol solution of **1**. Yield: 91%; ESI-MS: *m*/*z* = 348.20 $[Co(L1)(CH_3COO)]^+$; E *Anal.* Calc. for $[Co(L1)(CH_3COO)](PF_6){\cdot}H_2O$: C, 32.88; H, 6.90; N, 10.98. Found: C, 32.94; H, 6.93 N, 10.74%. IR spectroscopy: 3000(w), 1616(w), 1581(w), 1475(w), 1458(w), 1436(w), 1402(w), 1375(m), 1329(w), 1296(w), 1274(w), 1246(w), 1103(w), 1055(w), 1041(w), 1022(w), 1004 (w), 935(w), 910(w), 873(w), 831(s), 775(m), 740(w), 659(w), 555(s) and 484(w) cm^{-1}.

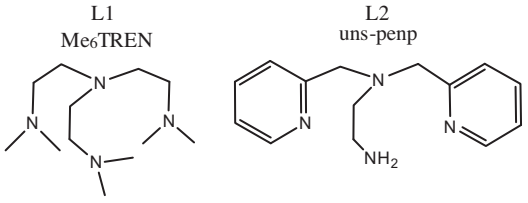

Fig. 1. Molecular structure of the ligands used in this study.

2.2. [Ni (L1)(CH_3COO)][PF_6]·H_2O (**2**)

$Ni(CH_3COO)_2$ (53 mg, 0,30 mmol) was dissolved in the smallest possible amount of methanol while an excess of Me_6TREN was dissolved in acetone. After addition of the second solution to the first one, a change in colour from light blue to green was observed. An excess of KPF_6, dissolved in acetone, was added to the previous solution in order to promote the anion metathesis reaction. The solvent was evaporated and the green solid obtained was dissolved in pure acetone. A white solid remained undissolved on the bottom of the flask (CH_3COOK) and was filtered off. The solution was dried under vacuum and the solid dissolved in dichloromethane in order to eliminate the excess of KPF_6. After filtration of the solid residue, the solution was reduced in volume and the pure product **2** was precipitated upon addition of *n*-pentane. Crystals suitable for XRD were grown at low temperature by slow diffusion of *n*-pentane into a dichloromethane solution of **2**. Yield: 86%; MALDI-TOF: *m*/*z* = 346.878 $[Ni(L1)(CH_3COO)]^+$; E *Anal.* Calc. for $[Ni(L1)(CH_3COO)](PF_6){\cdot}H_2O$: C, 32.90; H, 6.90; N, 10.96. Found: C, 33.23; H, 6.97; N, 10.93%. IR spectroscopy: 3000(w), 1616(w), 1581(w), 1475(w), 1458(w), 1436(w), 1406(w), 1377(m), 1330(w), 1290(w), 1257(w), 1093(m), 1039(w), 1018(s), 948(w), 935(w), 908(w), 873(w), 830(s), 802(s), 773(m), 738(w), 702(w), 683(w), 661(w), 555(s) and 476(w) cm^{-1}

2.3. [Ni (L2)(CH_3COO)][PF_6]·H_2O (**3**)

$Ni(CH_3COO)_2$ (218 mg, 0,43 mmol) was dissolved in the smallest possible amount of acetone and treated with an excess of uns-penp. The purple solution obtained was dried under vacuum and the oily purple residue was dissolved in acetone. An excess of KPF_6, dissolved in acetone, was added to the previous solution and a quick colour-change from purple to blue and then back to purple was observed together with the formation of the by-product CH_3COOK. After filtration, the acetone was evaporated and the purple precipitate was dissolved in dichloromethane in order to remove the excess of KPF_6. After filtration and reduction of the volume of solvent, **3** was precipitated out by slow addition of diethylether. Crystals suitable for XRD were grown at low temperature by slow diffusion of diethyl ether into a dichloromethane solution of **3**. Yield: 58%; ESI-MS: *m*/*z* 299.26 $[Ni(L2)]^{++}$, *m*/*z* = 359.25 $[Ni(L2)(CH_3COO)]^+$; E *Anal.* Calc. for $[Ni(L2)(CH_3COO)](PF_6){\cdot}CH_2Cl_2$: C, 36.82; H, 4.18; N, 10.10. Found: C, 37.39; H, 4.25; N, 10.66%. IR spectroscopy: 1608(w), 1573(w), 1541(w), 1481(w), 1444(w), 1415(w), 1348(w), 1311(m), 1290(w), 1159(w), 1099(w), 1080(w), 1051(w), 1022(w), 968(w), 877(w), 833(s), 761(w), 727(w), 680(w), 661(w), 646(w), 621(w), 617(w), 555(m) and 428(w) cm^{-1}.

Table 1
Crystal data, data collection and structure refinement for compounds **1**, **2**, **3** and **4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{28}H_{69}Co_2F_{12}N_8O_5P_2$	$C_{28}H_{68}F_{12}N_8Ni_2O_5P_2$	$C_{17}H_{23}Cl_2F_6N_4NiO_2P$	$C_{28}H_{66}Cu_2F_{12}N_8O_5P_2$
M_W (g mole^{-1})	1005.71	1004.26	589.97	1011.91
Crystal size (mm)	0.55 × 0.27 × 0.20	0.76 × 0.47 × 0.24	0.50 × 0.33 × 0.27	0.91 × 0.49 × 0.10
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a (Å)	8.30(1)	8.30(1)	8.55(1)	8.225(2)
b (Å)	16.45(2)	16.34(2)	10.78(1)	16.387(4)
c (Å)	32.353(4)	32.211(4)	13.40(1)	32.04(1)
α (°)	90	90	90.407	90
β (°)	97.318	97	105.517	96.673(8)
γ (°)	90	90	92.663	90
V (Å^3)	4378.8(8)	4336.3(1)	1189.5(2)	4289.5(18)
ρ_{calc} (g cm^{-3})	1.526	1.540	1.647	1.449
Z	4	4	2	4
μ (mm^{-1})	0.93	1.04	1.18	1.16
T (K)	300	300	300	200
Θ range (°)	2.3–23.5	2.3– 24.2	2.4–25.1	1.8; 19.7
Reflections collected	73920	63776	23351	23431
Unique reflections	6501	6929	4180	3829
Observed reflections [$I > 2\sigma(I)$]	4967	5621	3571	3165
Parameters refined/restraint	536	536	307	528
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan
T_{min}; T_{max}	0.63; 0.84	0.51; 0.79	0.59; 0.74	0.42; 0.89
σ_{fin} (max/min) [e Å^{-3}]	−0.86	−1.5	−1.06	−1,5
R_1 [$I \geqslant 2\sigma(I)$]	0.059	0.059	0.035	0.048
wR_2	0.169	0.159	0.091	0.122
CCDC number	913118	913119	913120	913121

2.4. [Cu (L1)(CH_3COO)][PF_6]·H_2O (**4**)

$Cu(CH_3COO)_2{\cdot}H_2O$ (52 mg, 0,26 mmol) was dissolved in the smallest possible amount of acetone and treated with an excess of Me_6TREN. The mixture was left under vigorous stirring for a couple of hours. During this time, the solution turned from blue to green. After evaporation of the solvents, the green product was redisolved in acetone and an excess of KPF_6 (dissolved in acetone as well) was added. The white solid CH_3COOK formed on the bottom of the flask and it was filtered off. The light blue solution was dried under vacuum and the solid dissolved in dichloromethane in order to eliminate the excess of KPF_6. After filtration of the solid residue, the solution was reduced in volume and the pure product **4** precipitated upon addition of diethylether. Crystals suitable for XRD were grown at low temperature by slow diffusion of diethyl ether into a dichloromethane solution of **4**. Yield: 27%; ESI-MS: m/z = 352,13 $[Cu(L1)(CH_3COO)]^+$; E *Anal.* Calc. for $[Cu(L1)(CH_3COO)](PF_6){\cdot}2H_2O$: C, 31.46; H, 6.93; N, 10.49. Found: C, 30.89; H, 6.89; N, 10.39%. IR spectroscopy: 3000(w), 1622(w), 1475(w), 1458(w), 1436(w), 1375(m), 1329(w), 1296(w), 1274(w), 1246(w), 1103(w), 1055(w), 1041(w), 1022(w), 1004 (w), 935(w), 910(w), 873(w), 831(s), 775(m), 740(w), 659(w), 555(s) and 484(w) cm^{-1}.

2.5. Catalytic oxygenations

All the catalytic oxygenation experiments have been carried out at room temperature under research grade nitrogen atmosphere. Typically, the concentration of the complex in solution was 0.35 mM, 0.30 M for the *m*-CPBA and 1.85 M for the organic substrate. As solvent, 8 mL of a mixture CH_3CN:CH_2Cl_2 (v/v 3/1 or v/v 1/3) has been used [10]. After 1 h, the reaction was quenched with triphenylphosphine and diluted 5 times using the same mixture of solvents. 1.5 μL of bromobenzene were added as internal standard. The solution was subjected to GC analysis using Perkin–Elmer 8500 GC. The products were detected by FID and quantified using a calibration curve obtained with authentic compounds. For the detection of the oxidation products of cyclohexanone, the GC was equipped with PoraPLOT Q capillary column (25 m × 0.32 mm × 210 μm) and the products were quantified in isothermal conditions. When the solvent mixture was CH_3CN:CH_2Cl_2 v/v 3/1, the temperature program was: injector temperature 250 °C; oven temperature 250 °C; FID temperature 250 °C, while, for the solvent mixture CH_3CN:CH_2Cl_2 v/v 1/3 the program was: injector temperature 250 °C; oven temperature 225 °C; FID temperature 250 °C. On the other hand, for the detection of the adamantane oxidation products the GC was equipped with an OPTIMA1 capillary column (25 m × 0.32 mm × 0.25 μm) and they were quantified using the following temperature program: injector temperature 130 °C; initial temperature 60 °C, heating rate 10 °C min^{-1} to 130 °C, increasing the temperature to 135 °C at a rate of 0.5 °C min^{-1}, and then increasing the temperature to 260 °C at a rate of 20 °C min^{-1}; FID temperature 280 °C. The average of four to six measurements is reported for each catalyst.

3. Results and discussion

3.1. Synthesis and characterization of the compounds

The tripodal tetradentate 4N ligands L1 and L2 are synthesized according to the procedures reported in literature [13]. The Ni(II), Co(II) and Cu(II) complexes are synthesized by reactions of $M(CH_3COO)_2$ (M = Ni(II), Co(II) or Cu(II)) with the ligands followed by a metathesis reaction between an acetate anion and a PF_6^- anion. The raw products are washed first with dichloromethane, in order to remove the excess of KPF_6, and then with diethyl ether, for removing the excess of ligand. This two-step procedure leads to the final products **1**, **2**, **3** and **4** that are fully characterised by elemental analysis, mass spectroscopy and single crystal X-ray diffraction. Attempts to synthesize Co/L2 and Cu/L2 derivatives did not lead to the isolation of pure materials.

3.2. Description of the X-ray crystal structures

Molecular structures of the complexes are reported in Fig. 2 while selected bond lengths and bond distances are collected in

Table 2. The compounds containing L1 are all isostructural and they crystallise in the monoclinic space group $P2_1/n$. Each unit cell contains two complex and anion molecules and one water molecule. For these three complexes, the acetate behaves as a monodentate ligand and the central M(II) is pentacoordinate with a trigonal bipyramidal geometry. The metal–oxygen distance decreases moving form nickel [1.966(4)/1.983(4) Å] to cobalt [1.964(4)/1.974(4) Å] to copper [1.912(5)/1.899(5) Å]. The apical nitrogen atom of the ligand (N_A) is always coordinated in the position trans to the oxygen atom, with angles ON_A of 174.4(1)°/169.8(1)° for cobalt, 172.9(1)°/170.3(1)° for nickel and 170.8(2)°/172.9(1)° for copper. The M–N_A is the shortest of all the M–N interactions for Cu [Cu–N_A 2.037(6)/2.023(5) vs. Cu–N_P 2.144(5)/2.148(6), 2.163(5)/2.156(5) and 2.140(5)/2.124(5) Å; N_P stands for peripheral amino nitrogen atoms], while it is the longest for the cobalt complex [CoN_A 2.199(3)/2.223(4) versus Co Ni–N_P 2.081(4)/2.098(4), 2.133(4)/2.141(4) and 2.136(3)/2.165(4) Å. The steric hindrance created by the six methyl groups of the ligand L1 prevents the coordination of one further ligand molecule, hampering the preferred octahedral coordination environment of the metal atoms. Complex **3** bears the ligand L2 and it crystallises in the trigonal space group $P\bar{1}$. The acetate ligand is coordinated in a slightly asymmetric (η^2) manner with Ni–O bond distances of 2.193(2) and 2.060(2) Å for NiO1 and NiO2, respectively, leading to a complex with an octahedral geometry. The longest M–N bond in this complex is the one involving the apical nitrogen atom N_A [NiN_A 2.078(2) vs. NiN_P 2.062(3), 2.056(2) and 2.061(2) Å]. For all the compounds bond angles deviate from the ideal trigonal bipyramidal or octahedral geometry, revealing the presence of significant distortion in the metal coordination geometry.

3.3. Catalytic oxidation of alkanes

The catalytic activity of the three L1 derivatives towards oxidation of alkanes such as cyclohexane and adamantane is explored by using *m*-CPBA as the oxidant in an acetonitrile/ dichloromethane solvent mixture at room temperature and under nitrogen atmosphere. The reactivity and selectivity parameters for alkane conversion are summarized in Tables 3–5. The conversion of alkanes into hydroxylated products was quantified based on gas chromatographic analysis by using authentic samples and an internal standard. It has been reported that *m*-CPBA is a very strong oxidising agent for the oxidation of hydrocarbons to the corresponding alcohols and ketones in the absence of any metal catalyst, but usually under vigorous reaction conditions including very high concentrations of *m*-CPBA, long reaction times and high temperatures [16]. Therefore, control experiments in the absence of the metal complexes have been performed. With *m*-CPBA alone, no oxidation

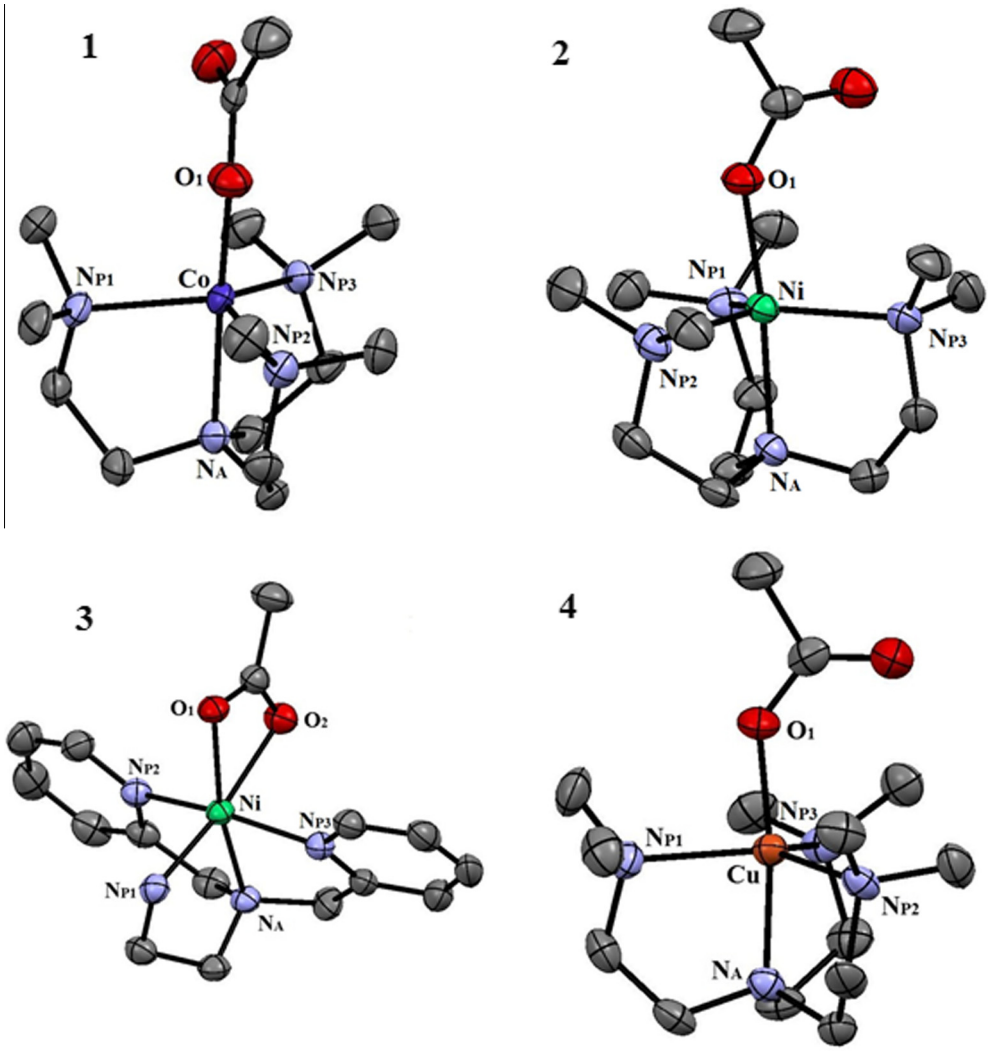

Fig. 2. Molecular structures of $[Co(L1)(CH_3OO)]^+$ (**1**), $[Ni(L1)(CH_3OO)]^+$ (**2**), $[Ni(L2)(CH_3OO)]^+$ (**3**) and $[Cu(L1)(CH_3OO)]^+$ (**4**) (50% probability factor for the thermal ellipsoids). Hydrogen atoms have been omitted for clarity.

Table 2
Selected bond lengths [Å] and bond angles [°] for complexes **1**, **2**, **3** and **4.**

	1 (M = Co(II))[a]	**2** (M = Ni(II))[a]	**3** (M = Ni(II))[b]	**4** (M = Cu(II))[a]
Bond lengths (Å)				
M–N_A	2.199(3)	2.098(4)	2.078(2)	2.037(6)
	2.223(4)	2.099(3)		2.023(5)
M–N_{P1}	2.144(4)	2.081(4)	2.062(3)	2,144(5)
	2.166(4)	2.098(4)		2.148(6)
M–N_{P2}	2.134(4)	2.133(4)	2.056(2)	2.163(5)
	2.133(4)	2.141(4)		2.156(5)
M–N_{P3}	2.142(4)	2.136(3)	2.061(2)	2.140(5)
	2.147(4)	2.165(4)		2.124(5)
M–O_1	1.964(3)	1.966(4)	2.193(2)	1.912(5)
	1.974(4)	1.983(4)		1.899(5)
M–O_2	3.524	3.514	2.060(2)	3.219
	3.177	3.230		3.433
Bond angles (°)				
O_1–M–N_A	174.4(1)	172,9(1)	103.6(1)	170.8(2)
	169.8(1)	170.3(1)		172.9(1)
O_1–M–N_{P1}	93.2(1)	99.9(1)	170.5(1)	100.8(2)
	89.7(2)	101.6(1)		97.3(2)
O_1–M–N_{P2}	100.7(1)	98.5(1)	87.0(1)	86.8(2)
	104.6(1)	99.8(1)		88.0(2)
O_1–M–N_{P3}	102.3(1)	89.2(1)	88.9(1)	99.0(2)
	103.6(1)	88.1(1)		100.4(2)
N_A–M–N_{P1}	81.3(1)	85.0(1)	85.9(1)	84.6(2)
	80.1(2)	84.6(2)		84.5(2)
N_A–M–N $_{P2}$	81.4(1)	84.1(1)	80.9(1)	84.1(2)
	81.1(1)	83.9(2)		85.0(2)
N_A–M–N_{P3}	81.1(1)	83.7(1)	82.5(1)	84.7(2)
	80.8(1)	82.5(1)		84.7(2)
N_{P1}–M–N_{P2}	116.9(1)	115.3(1)	95.8(1)	118.2(2)
	116.8(2)	115.6(2)		117.1(2)
N_{P1}–M–N_{P3}	119.2(1)	113.9(1)	91.2(1)	118.1(2)
	118.9(2)	114.7(2)		118.0(2)
N $_{P2}$–M–N_{P3}	117.2(1)	127.7(1)	161.5(1)	121.0(2)
	116.6(1)	126.2(2)		122.4(2)
O_2–M–N_A			165.55(8)	
O_2–M–N_{P1}			108.53(8)	
O_2–M–N $_{P2}$			96.59(8)	
O_2–M–N_{P3}			97.39(8)	
O_2–M–O_1			62.01(7)	

[a] For the pentacoordinate L1 complexes **1**, **2** and **4**: O_1 is the oxygen of the acetate group which is bound to the metal centre, while O_2 is the uncoordinated one. N_A is the apical nitrogen atom of the ligand, the one bound to the three $–CH_2CH_2N(CH_3)_2$ groups and N_{P1}, N_{P2} and N_{P3} are the peripheral nitrogen atoms, each one bound to an ethylene group and two $–CH_3$ groups.
[b] For complex **3**: N_A is the apical nitrogen atom of the ligand; N_{P1} is the nitrogen atom of peripheral $–NH_2$ group; N_{P2} and N_{P3} are the pyridine nitrogen atoms.

Table 3
Conversion of cyclohexane catalysed by complexes **1**, **2** and **4**. Solvent CH_3CN:CH_2Cl_2 (v/v 3/1).[a]

Complex	Cyclohexane (TON)			A/K[c]
	Cyclohexanol (A)	Cyclohexanone (K)	Total TON[b]	
1	177	61	237	2.9
2	5	5	10	1
4	0	0	0	–

[a] Reaction conditions: catalyst (0.35×10^{-3} M), substrate (1.85 M), *m*-CPBA (0.30 M) in CH_3CN:CH_2Cl_2 (v/v 1/3).
[b] Total TON = mmol of products/mmol of catalyst.
[c] Selectivity A/K = TON (cyclohexanol)/TON (cyclohexanone).

Table 4
Conversion of cyclohexane catalysed by complexes **1**, **2** and **4**. Solvent CH_3CN:CH_2Cl_2 (v/v 1/3).[a]

Complex	Cyclohexane (TON)			A/K[c]
	Cyclohexanol (A)	Cyclohexanone (K)	Total TON[b]	
1	62	6	68	10.3
2	29	3	31	9.1
4	0	0	0	–

[a] Reaction conditions: catalyst (0.35×10^{-3} M), substrate (1.85 M), *m*-CPBA (0.30 M) in CH_3CN:CH_2Cl_2 (v/v 1/3).
[b] Total TON = mmol of products/mmol of catalyst.
[c] Selectivity A/K = TON (cyclohexanol)/TON (cyclohexanone).

products have been detected when cyclohexane is the substrate, while a certain amount of both 1-adamantanol and 2-adamantanol have been detected when adamantane is used as a substrate. The amount of products generated in the latter case has been taken into account for the calculation of corrected TONs, in order to avoid any overestimation of the catalytic activity of the systems under investigation. With cyclohexane as a substrate, catalytic oxidation in the presence of the L1 transition metal complexes **1** and **2** results in the formation of cyclohexanol as the major product, along with cyclohexanone as the minor product. It is well known that *m*-CPBA can act as a quantitative reagent for the conversion of cyclic ketones to the corresponding lactones (Bayer-Villiger oxidation), which occurs in the absence of any metal catalyst. Moreover, Palaniandavar et al. [10c] reported the presence in the reaction mixture of ε-caprolactone as the over-oxidised product of the oxidation of cyclohexanone by *m*-CPBA. However, in our case, the GC chromatograms of the studied solutions do not show any other product peaks beside the signatures of cyclohexanol and cyclohex-

Table 5
Conversion of adamantane catalysed by complexes **1**, **2** and **4**. Solvent CH_3CN:CH_2Cl_2 (v/v 1/3).[a]

Complex	Adamantane oxidation (TON)[b]				Selectivity 3°/2°[c]
	1-adamantanol	2-adamanatanol	2-adamantanone	Total TON	
1	68	8	26	102	6
2	12	0	0	12	–
4	0	0	0	0	–

[a] Reaction conditions: catalyst (0.35×10^{-3} M), substrate (1.85 M), *m*-CPBA (0.30 M) in CH_3CN:CH_2Cl_2 (v/v 1/3).
[b] Total TON = mmol of products/mmol of catalyst.
[c] Selectivity 3°/2° = 3 × TON(1-adamantanol)/(TON(2-adamantanol) + TON(2-adamantanone)).

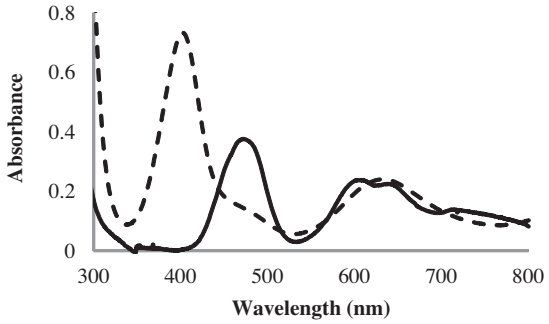

Fig. 3. UV–Vis spectra of complexes **1** (solid line) and **2** (dashed line) in acetonitrile.

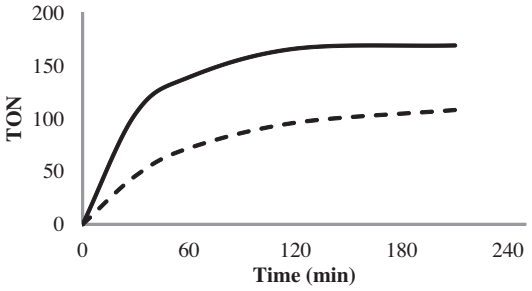

Fig. 4. Time dependency of TON for oxidation of cyclohexane catalysed by **1** with *m*-CPBA. Solid line: TON variation for cyclohexanol; dashed line: TON variation for cylohexanone.

anone. The production of ε-caprolactone can therefore be ruled out under these reaction conditions.

When the oxidative reaction is carried out in CH_3CN:CH_2Cl_2 (v/v 3/1) as a solvent mixture, the cobalt catalyst **1** shows an interesting catalytic activity for the oxidation of cyclohexane with a TON of 177 for cyclohexanol (A) and 61 for cyclohexanone (K) (A/K = 2.9) (Table 3). Complex **2**, on the other hand, is a very poor catalyst for this reaction with TONs of 5 for both the products (A/K = 1). By modifying the reaction medium to a less polar solvent mixture CH_3CN:CH_2Cl_2 (v/v 1/3), a dramatic variation of the catalytic properties for **1** is observed. In fact, the TONs decrease (TON of 62 for cyclohexanol (A) and 6 for cyclohexanone (K)) but the reaction becomes much more selective with A/K of 10.3 (Table 4). Complex **2** is a better catalyst in this solvent mixture than in the more polar medium, with a TON of 29 for cyclohexanol and 3 for cyclohexanone. Also the selectivity of **2** is improved with a ratio A/K of 9.1. Interestingly, we found that the copper derivative **4** does not catalyse the same reaction under any of the tested conditions, which seems to indicate that a catalytically competent $[CuO^{\cdot}]^{+}$ intermediate, which should be capable of selective C–H bond activation [11], obviously cannot be obtained starting from *m*-chlorobenzoic acid oxidation with this complex. Itoh et al. proposed a mechanism [10] for a Ni(II) complex carrying tripodal tetradentate ligands, in which *m*-CPBA binds to the Ni(II)-atom in the catalytically active species $[(L)Ni(X)(X_1)]$ to give $[(L)Ni(X)(OOC(O)Ar)]$ (L is the tetradentate supporting ligand, X and X_1 are the coordinated counter anion and/or the phenolate moiety involved in L and Ar is *m*-chlorophenyl group). This intermediate, subsequently, undergoes O–O bond homolysis leading to the formation of a highly reactive nickel-oxo species and a *m*-chlorobenzoic acid radical. A metal-oxo species of the type $[(L)(X)Ni–O^{\cdot}]^{+}$ carrying an electrophilic oxyl radical character would then be involved in the selective hydroxylation of alkanes, while the *m*-chlorobenzoic acid radical undergoes decarboxylation to form chlorobenzene [10b]. The observation of chlorobenzene supports the involvement of the intermediate species $[(L)(X)Ni–O^{\cdot}]^{+}$ in the catalysis and indicates that the *m*-chlorobenzoate radical is not the reactive intermediate, because it readily undergoes decarboxylation rather than hydrogen abstraction from the alkane. The formation of a similar nickel-oxo species as an intermediate in this kind of reactions has been recently reported by Pfaff et al. [17]. With the aim of better understanding nickel-based C–H hydroxylations and oxygen-transfer processes, this group investigated the reaction between $[Ni(TMG_3tren)(OTf)]$ (TMG_3tren = tris[2-(*N*-tetramethylguanidyl)ethyl] amine, OTf = triflate) and *m*-CPBA. UV–Vis and EPR measurements supported their hypothesis that the intermediate is a Ni^{III}-oxo/hydroxo species.

In our case, furthermore, the tetradentate ligand L1 prevents the formation of a bis-substituted complex such as the one observed by Itoh [10], since the steric hindrance created by the six methyl groups is quite high [18]. We therefore infer that the catalytically active species in these systems is, in contrast, a mono-substituted derivative, which is supported by UV–Vis. In particular, when the complexes are dissolved in acetonitrile, the coordinated acetate group can be replaced by a solvent molecule leading to the formation of the mono-acetonitrile species $[(L)M(CH_3CN)]^{2+}$, which is characterised by a long wavelength absorption band pattern between 600 and 700 nm in the UV–Vis spectra [18] (Fig. 3). When a solvent mixture rich in acetonitrile is used, the catalytic activity of the Ni complex **2** is reduced. This behaviour may be simply due to the fact that a coordinating solvent competes with the *m*-CPBA for binding to the only free coordination site. On the other hand, an opposite behaviour is observed for the cobalt derivative, which indicates that a different mechanism is followed by this system. Although at the present stage of investigations the discussion of a more detailed picture is certainly not justified, it is tempting to ascribe the reactivity differences between the cobalt and nickel catalysts and their pronounced dependency on variations of the reaction medium to a possible switch in the O–O bond cleavage mechanism of the peroxo intermediates involved. As observed before with other transition metal complexes, a one-electron change in the *d*-electron configuration may induce a drastic change of reactivity from peroxo bond homolysis to heterolytic bond cleavage [19]. Furthermore, homolysis is facilitated in a less polar reaction medium, while increasing the solvent mixture polarity may favour a heterolytic O–O bond cleavage [20]. Taking together our experimental results and the recent data published in the literature

[17], it seems plausible that heterolytic peroxo bond cleavage is operating in the cobalt case **1**, while the catalytic oxidations with the nickel system **2** are following a homolytic pathway.

Since the cobalt catalyst **1** shows the highest catalytic activity in the more polar solvent mixture CH_3CN:CH_2Cl_2 (v/v 3/1), the time course of the TONs in cyclohexane oxidation has been investigated under these conditions and the dependency is shown in Fig 4. The catalytic activity of the cobalt complex for both of the products increases even after 1 h. Cyclohexanol remains the major product during the all course of the experiment but, after 1 h, the increase of TON is more pronounced for cyclohexanone than for the alcohol.

Oxidation of adamantane has been carried out under the same reaction conditions as described for cyclohexane, but only the solvent mixture CH_3CN:CH_2Cl_2 (v/v 1/3) could be used since adamantane is not soluble in acetonitrile and most of the substrate remains undissolved when a more polar solvent is employed. Compound **1** is a good catalyst even with this substrate with TONs of 68 for 1-adamantanol, 8 for 2-adamantanol and 26 for 2-adamantanone, but the selectivity is still quite low (3°/2° = 6) (see Table 5). Compound **2**, on the other hand, has quite a low TON of 12 for the production of 1-adamantanol, which is the only product observed. The copper derivative **4** is, once again, not active as a catalyst. It is important to point out, that *m*-CPBA alone as a strong oxidant in principle can lead to a similar oxidation reaction, so the detected concentration of all the products is actually higher than the one used here for the corrected TON calculations.

4. Conclusions

In this paper, four new complexes containing the well-known tripodal tetradentate 4N ligands tris[2-(dimethylamino) ethyl]amine (Me_6TREN, L1) and (2-aminoethyl)bis(2-pyridylmethyl) amine (uns-penp, L2) have been isolated and fully characterised. The only L2 complex that has been isolated is the nickel derivative **3** and it has the general formula [Ni(L2)(CH_3COO)][PF_6]. The ligand L2 is not very robust and, as a consequence, the complex turned out not to be very stable under substrate oxidation conditions. Therefore, the catalytic activity measurements reported here were restricted to the series of new L1 metal complexes. All the L1 derivatives have a general formula [M(L1)(CH_3COO)][PF_6] [M = Co(II), Ni(II), Cu(II)] and are pentacoordinate in the solid state, with only one of the acetate oxygen atoms coordinated to the metal centre. The cobalt and nickel derivatives of L1 have been found to catalyse the hydroxylation of both cyclohexane and adamantane in the presence of *m*-CPBA as an oxidant with good selectivity and TON values. In particular, the cobalt derivative **1** is the catalyst with the highest TONs reached, while the nickel complex **2** is the most selective catalyst for partial alkane oxidation at room temperature in homogeneous solution. The corresponding copper L1 derivative **4**, however, does not show any catalytic activity for alkane oxidation under the same reaction conditions.

Acknowledgments

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Appendix A

CCDC 913118–913121 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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